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BIODEGRADABLE POLYESTER AMIDES WITH ALIPHATIC-AROMATIC  
STRUCTURES

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The following information has been taken from the documents submitted by the applicant

Randomly constructed biodegradable aliphatic-aromatic polyester amides that consist of the following monomers:

aliphatic diols such as ethylene glycol, diethylene glycol, 1,4-butanediol, 1,3-propanediols, 1,6-hexanediol or cycloaliphatic diols such as cyclohexanedimethanol, and/or

aliphatic dicarboxylic acids such as oxalic acid, succinic acid, adipic acid, among others also in the form of their esters (methyl-, ethyl-, etc.), and/or

aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, phthalic acid, among others also in the form of their esters (methyl-, ethyl-, etc.), and/or

hydroxycarboxylic acids and lactones such as caprolactone among others, and/or

amino alcohols such as ethanolamine, propanolamine, etc., and/or

cyclic lactams such as  $\epsilon$ -caprolactam, lauric lactam etc. and/or

$\omega$ -aminocarboxylic acids such as amino caproic acid etc, and/or

Mixtures (1:1 salts) of dicarboxylic acids such as adipic acid, succinic acid, terephthalic acid, etc., and diamines such as hexamethyldiamines, diaminobutane etc., containing up to 70 mol% (regarding the acid portion) of aromatic dicarboxylic acids.

Decomposable aliphatic polyester amides are known (e.g., EP-A 545 203 and 641 817).

Decomposable aliphatic-aromatic polyester amides are also known (WO 92/21689, WO 96/21690, WO 96/21691 and WO 96/21692).

In these patents polyester amides from adipic acids and hydroxycarboxylic acids are described which must yet be crosslinked in order to attain sufficient mechanical characteristics. This crosslinking is accomplished via diisocyanates, divinyl ether or bisoxazolines.

However, this reaction is very complex and difficult to control. There is always the risk of uncontrolled crosslinkages, which may lead to the formation of gel bodies in later processing or similar phenomena. These gel bodies are particularly undesirable in the production of films, however, as highly crosslinked components they also inhibit biological decomposition.

It is the task of the present invention to provide aliphatic-aromatic polyester amides that are composed randomly and do not feature the above-mentioned disadvantage.

The objects of the invention are therefore randomly composed aliphatic-aromatic polyester amides which consist of the following monomers:

- aliphatic diols such as ethylene glycol, diethylene glycol, 1,4-butanediol, 1,3-propanediols, 1,6-hexanediol or cycloaliphatic diols such as cyclohexanedimethanol, and/or
- aliphatic dicarboxylic acids such as oxalic acid, succinic acid, adipic acid, among others, also in the form of their esters (methyl-, ethyl-, etc.), and/or
- aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, phthalic acid, among others, also in the form of their esters (methyl-, ethyl-, etc.), and/or
- hydroxycarboxylic acids and lactones such as caprolactone, among others, and/or
- amino alcohols such as ethanolamine, propanolamine, etc., and/or
- cyclic lactams such as  $\epsilon$ -caprolactam, lauric lactam, etc., and/or
- $\omega$ -aminocarboxylic acids such as aminocaproic acid etc. and/or

- Mixtures (1:1 salts) of dicarboxylic acids such as adipic acid, succinic acid, terephthalic acid etc., and diamines such as hexamethyldiamines, diaminobutane etc.,

containing up to 70 mol% (regarding the acid portion) of aromatic dicarboxylic acids.

Preferably, the polyester amides contain 0.5-65 mol% of aromatic dicarboxylic acids.

The objects of the invention are, further, the use of the above-mentioned polyester amides for the production of films, sheets, injection-molded parts, nonwoven fabrics, fibers and foams as well as produced films, sheets, injection-molded parts, nonwoven fabrics, fibers and foams.

Likewise, hydroxyl- or acid-terminated polyesters from the described monomers with molecular weights between 300 and 10,000 may both be used as ester-forming components.

Likewise, amino- or acid-terminated polyesters from the described monomers with molecular weights between 200 and 10,000 may be used as amide-forming components.

The synthesis may be performed both according to the "polyamide method" by way of stoichiometric blending of the initial components, possibly adding water and subsequently removing the water from the reaction mix, and also according to the "polyester method" by way of adding an excess amount of diol with esterification of the acid groups and subsequent transformation of the esterification or reamidation of these esters. In this second instance, aside from the water, also the excess glycol is distilled off again.

In the synthesis, caprolactam or AH-salts or blends thereof with butanediol and diethylene glycol and a blend of terephthalic acid and adipic acid are preferably used.

The polyester amides produced in this manner are completely biodegradable according to DIN 54 900 and feature very good mechanical characteristics making it unnecessary to crosslink them subsequently.

The term enzymatic biodegradability characterizes the property of polymers of being decomposed by enzymes. In this process, the linkages by which the polymer units are connected together are split. As a decomposition product, the monomers of the polymer are formed as well as their oligomers. The enzymatic decomposition of the polymer reduces its molecular weight. Enzymatic decomposition differs from biodegradation in that it usually will not result in decomposition products which exist in nature.

As enzymes which decompose biodegradable polymers, basically those can be used which are capable of splitting the linkages contained in the polymer. Care must be taken when selecting the enzymes to make sure that they are capable of decomposing the polymer quickly and completely. The decomposition is performed in an aqueous solution which may be buffered. The pH-value may range between 3 and 11, preferably between 5 and 9 and particularly preferably is between 6 and 8. The temperature at which the enzymatic decomposition is performed may range between 5 and 95°C, preferably between 20 and 70°C and particularly preferably between 30 and 50°C.

The following buffers can be used according to the invention: citrate, acetate, phosphate, formate, carbonate, trihydroxymethylaminomethane, triethanolamine, imidazole, oxalate, tartrate, fumarate, maleate, phthalate, succinate, ethylenediamine and blends of them. Preferred buffers are acetate, phosphate and citrate.

One proceeds in such a manner that enzyme and polymer are added to the aqueous solution. The biodegradable polymer may be added as a film, as a sheet or as granulate. Molded parts may be added as a whole or comminuted. Coated or glued materials or such materials on which coatings have been applied using biodegradable polymers or on which biodegradable polymers have been used to apply layers or to glue parts together such as, e.g., paper or cardboard as well as laminated paper or laminated cardboard may be added to the enzyme-containing solution as a whole or comminuted.

Furthermore, the aqueous enzyme-containing solution may be applied or sprayed on the coating or the molded piece to be decomposed.

Lipolytic and proteolytic enzymes may be used as enzymes.

In this invention, lipases, cutinases, esterases, phospholipases and lysophospholipases are defined as lipolytic enzymes. The lipolytic enzymes are preferably derived from microorganisms. They are in particular derived from bacteria, fungi and yeasts. In addition, the lipolytic enzymes may also be derived from plant or animal sources.

In this invention, proteases are defined as proteolytic enzymes. Preferably, these are derived from bacteria of the genus *Bacillus* and particularly preferred are the proteases of the organisms *Bacillus alcalophilus* and *Bacillus licheniformis*. They may also be derived from fungi or plants.

The joint use of lipolytic and proteolytic enzymes as well as of lipolytic enzymes of differing specificity, which may generate synergistic effects, is in accordance with the invention. Further in accordance is the addition of metal ions such as sodium ions or calcium ions, which accelerate the enzymatic decomposition. The addition of anionic or nonionic surfactants such as, e.g., secondary alcohol ethoxylates is also in accordance with the invention.

Compostability is the characteristic of a polymer material of being decomposed biologically during a composting process. In order to be considered compostable, proof must be provided using standardized methods that the polymer material can actually be biologically decomposed in a composting system and that a qualitatively acceptable compost (according to DIN 54 900) can be produced.

The biological degradation of a material is a process caused by biological activity which, by altering the chemical structure of the material, leads to naturally occurring metabolic end-products (DIN 54 900).

A polymer material is biodegradable if all of its organic components can be completely biodegraded as defined by standardized processes (according to DIN 54 900).

Appropriate catalysts can be used in the production of polyester amides for the catalysis of the esterification reactions or of the amidation reactions. These catalysts are state of the art. However, they must not subsequently obstruct the use of the decomposable polymer as compost or interfere with the biodegradation processes. For this reason, the use of catalysts based on heavy metals such as lead or antimony has been completely excluded.

The blends according to the invention may additionally contain 0-80 wt% of customary additives, e.g., inorganic fillers or reinforcing agents, preferably fibrous (fiberglass, carbon fiber) and mineral fillers (e.g., talc, mica, chalk, kaolin, wollastonite, gypsum, quartz, dolomite, etc.), UV stabilizers, antioxidants, pigments, colorants, nucleating agents, crystallization accelerators or inhibitors, antiblocking agents, slip additives, mold-release agents, flameproofing agents.

The polyester amides according to the invention may also contain 0.05-5 wt%, preferably 0.1-1 wt% of branching agents. These branching agents could, e.g., be trifunctional alcohols such as pentaerythrite, trifunctional carboxylic acids such as citric acid, or also trifunctional or tetrafunctional hydroxycarboxylic acids.

## Examples

### Example 1

1233.8 g (2.066 mol) caprolactam, 58.1 g (0.397 mol) adipic acid, 89.4 g (0.992 mol) butanediol and 65.99 g (0.397 mol) terephthalic acid are heated together under nitrogen to 250°C. After 1 h, a water-jet vacuum is applied and after 2.5 h, an oil-pump vacuum [is applied] and water and butanediol are distilled off. After 7 h of polycondensation time, one obtains a colorless polymer with a melting point of 136°C.

The material is completely decomposable according to DIN 54 900.

### Example 2

2185.8 g (0.709 mol) AH salt, 156.9 g (1.074 mol) adipic acid, 24.7 g (0.274 mol) butanediol, 95.9 g (0.904 mol) diethylene glycol and 9.39 g (0.057 mol) terephthalic acid are heated together under nitrogen to 250°C. After 1 h, a water-jet vacuum is applied, and after 2.5 h, an oil-pump vacuum, and water and butanediol are distilled off. After 7 h of polycondensation time, one obtains a colorless polymer with a melting point of 175°C.

The material can be completely decomposed according to DIN 54 900.

### Claims

1. Randomly composed aliphatic-aromatic polyester amides, which consist of the following monomers:

- aliphatic diols such as ethylene glycol, diethylene glycol, 1,4-butanediol, 1,3-propanediols, 1,6-hexanediol or cycloaliphatic diols such as cyclohexanedimethanol, and/or
- aliphatic dicarboxylic acids such as oxalic acid, succinic acid, adipic acid, among others, also in the form of their esters (methyl-, ethyl-, etc.), and/or
- aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, phthalic acid, among others, also in the form of their esters (methyl-, ethyl-, etc.), and/or
- hydroxycarboxylic acids and lactones such as caprolactone, among others, and/or
- amino alcohols such as ethanolamine, propanolamine, etc., and/or
- cyclic lactams such as  $\epsilon$ -caprolactam, lauric lactam, etc., and/or
- $\omega$ -aminocarboxylic acids such as aminocaproic acid, etc., and/or
- Mixtures (1:1 salts) of dicarboxylic acids such as adipic acid, succinic acid, terephthalic acid, etc., and diamines such as hexamethyldiamine, diaminobutane etc., containing up to 70 mol% (regarding the acid portion) of aromatic dicarboxylic acids.

2. Use of polyester amides according to Claim 1 for the production of films, sheets, molded parts, nonwoven fabrics, fibers and foams.

3. Films, sheets, molded parts, nonwoven fabrics, fibers, and foams produced from polyester amides according to Claim 1.